Journal of Thermal Analysis, Vol. 38 (1992) 1365-1376

STEREOCHEMISTRY AND THERMAL BEHAVIOUR OF NEW COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 5-(2-THIAZOLYLAZO)-BARBITURIC AND THIOBARBITURIC ACIDS AT DIFFERENT TEMPERATURES

M. S. Masoud[*a], S. A. Abou El-Enein[b] and O. F. Hafez[a]*

[a] CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY, ALEXANDRIA, EGYPT
[b] CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, MENOUFIA UNIVERSITY, SHEBIN EL-KOME, EGYPT

(Received May 31, 1991)

The stereochemistry of new cobalt(II), nickel(II) and copper(II) complexes of 5-(2-thiazolylazo)-barbituric and thiobarbituric acids was studied on the basis of thermal mea-surements. The orders of reactions and the energies of activation were evaluated. The data were explained from different aspects, mainly with regard to the electronic character of the substituent.

Keywords: complexes, stereochemistry

Introduction

Thiazolylazo and pyrimidine compounds have many applications, e. g. they are hypnotic drugs, they affect the nervous system [1], they are applied in the fight against gastric cancer [2], they are chemotherapeutic agents and they are involved in the structure of the nucleic acid in living systems. Some of the thiazolylazo compounds have been used as chromogenic-spectro-photometric and

---

* Author to whom correspondence should be directed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

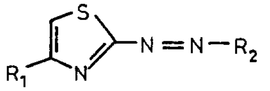
extraction reagents for the determination of many metal ions [3-8] and as indicators in complexometric titrations [9-13].

The structural chemistry of synthesized cobalt(II), nickel(II) and copper(II) complexes of barbituric acid and its azo derivatives was explained on the basis of spectral and magnetic susceptibility measurements [14]. Few of these systems were investigated from the aspect of their thermal properties. No work has been reported on the thermal properties of the complexes of 5-(2-thiazolylazo)-barbituric acid, 5-(4-phenyl-2-thiazolylazo)-barbituric acid, 5-(2-thiazolylazo)-2-thiobarbituric acid and 5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid with different metal ions such as Co(II), Ni(II) and Cu(II). Accordingly in the present work, DTA data are applied to evaluate the activation energies and orders of reactions of these complexes in order to shed light on their structural chemistry.

Experimental

The organic compounds were prepared by dissolving 2-aminothiazole and its 4-phenyl derivative (0.1 mole) in HCl (0.2 mole/25 ml distilled H_2O). The hydrochloride compounds were diazotized below 5 °C with a solution of $NaNO_2$ (0.1 mole/30 ml distilled H_2O). The diazonium chlorides [15] were coupled with an alkaline solution of barbituric or thiobarbituric acid (0.1 mole). The crude dyes were collected by filtration, crystallized from ethanol [16] and then dried over P_4O_{10} in a vacuum desiccator.

The C, H, N and S contents were analysed at the microanalytical units, Chemistry Department, Faculty of Sciences, Alexandria and Cairo Universities (Table 1). The elemental analyses indicated the existence of the following compounds:



R_1= H	R_2= barbituric acid
Ph	barbituric acid
H	2-thiobarbituric acid
Ph	2-thiobarbituric acid

The complexes of these compounds were prepared by refluxing an ammoniacal solution of the metal(II) chloride (M = Co, Ni and Cu) (0.01 mole) with an ammoniacal solution of the organic compound (0.01 mole) for ≈2 hours. The precipitated complexes were separated by filtration, washed with ethanol and dried over anhydrous $CaCl_2$ in a desiccator. All the complexes had melting point >300 °C. The C, H, N and S contents of the complexes were determined by EDTA complexometric titration [17]. The data are given in Table 2.

Table 1 Analytical data and some physical properties of the organic compounds

Compound	Colour	m. p. / °C	Calculated (Found) / %			
			C	H	N	S
5-(2-thiazolylazo)-barbituric acid	yellowish brown	170	35.1	2.1	29.3	13.4
			(34.9)	(2.0)	(29.2)	(13.3)
5-(4-phenyl-2-thiazolylazo)-barbituric acid	deep violet	182	49.6	2.8	22.2	10.1
		dec.	(49.5)	(2.8)	(21.9)	(10.0)
5-(2-thiazolylazo)-2-thiobarbituric acid	brown	166	32.9	1.9	27.4	25.1
		dec.	(32.7)	(1.8)	(27.2)	(24.8)
5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid	deep brown	120	47.1	2.7	21.1	19.3
			(46.8)	(2.6)	(20.9)	(19.1)

Table 2 Analytical data of the prepared complexes

Compound	Stoichiometry	Calculated (Found) / %				
		C	H	N	S	M
5-(2-thiazolylazo)-barbituric acid						
Co(II) complex	$ML \cdot 2H_2O$	25.3	2.1	20.1	9.6	17.7
		(25.1)	(2.0)	(19.9)	(9.6)	(17.7)
Ni(II) complex	$M_2L \cdot 6H_2O$	18.2	3.3	15.1	6.9	25.3
		(18.2)	(3.1)	(15.0)	(6.7)	(25.1)
Cu(II) complex	$ML_2 \cdot 2H_2O$	29.1	2.1	24.3	11.1	11.0
		(29.0)	(2.1)	(24.1)	(11.0)	(11.0)
5-(4-phenyl-2-thiazolyl-azo)-barbituric acid						
Co(II) complex	$ML \cdot 2H_2O$	38.2	2.7	17.1	7.8	14.4
		(38.0)	(2.6)	(17.0)	(7.7)	(14.3)
Ni(II) complex	$ML_2 \cdot 4H_2O$	41.1	3.2	18.4	8.4	7.7
		(40.9)	(3.1)	(18.2)	(8.3)	(7.7)
Cu(II) complex	$ML_2 \cdot 4H_2O$	40.8	3.1	18.3	8.4	8.4
		(40.7)	(3.1)	(18.1)	(8.4)	(8.3)
5-(2-thiazolylazo)-2-thiobarbituric acid						
Co(II) complex	$ML \cdot 2H_2O$	24.1	2.0	20.1	18.4	16.9
		(24.1)	(1.9)	(20.1)	(18.3)	(16.9)
Ni(II) complex	$M_2L \cdot 6H_2O$	17.5	3.1	14.6	13.4	24.5
		(17.3)	(3.0)	(14.5)	(13.4)	(24.4)
Cu(II) complex	$ML_2 \cdot 2H_2O$	27.5	1.9	23.0	21.1	10.4
		(27.4)	(1.7)	(23.0)	(21.0)	(10.4)

Table 2 Continued

Compound	Stoichiometry	Calculated (Found) /%				
		C	H	N	S	M
5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid						
Co(II) complex	$ML \cdot 2H_2O$	36.7	2.6	16.5	15.1	13.8
		(36.5)	(2.5)	(16.4)	(15.0)	(13.8)
Ni(II) complex	$ML_2 \cdot 4H_2O$	39.4	3.0	17.6	16.2	7.4
		(39.4)	(3.0)	(17.4)	(16.0)	(7.4)
Cu(II) complex	$ML_2 \cdot 2H_2O$	39.2	3.0	17.6	16.1	7.9
		(39.0)	(2.8)	(17.5)	(16.0)	(7.8)

*All the metal-complexes are brown in colour with melting points > 300°C

The differential thermal analysis measurements were made with a Heraeus DTA 500 analyser, using a Ni-Cr-Ni temperature sensor, at the Postgraduate Research Institute, Alexandria University. The heating rate used was 10 deg·min^{-1}, with a 60 mg sample in a platinum crucible.

Results and discussion

The DTA curves of the cobalt, nickel and copper complexes are recorded in Fig. 1. An endothermic peak appears in the temperature range 46°-166 °C and can be assigned to the dehydration of the complexes [18, 19]. The energies of activation (ΔE_a) of the process of dehydration of these complexes were evaluated with a Piloyan *et al.* method [20] (Fig. 2). In turn, the order values (n) were calculated via the peak asymmetry method of Kissinger [21]. The ΔE and n values are given in Table 3. The data relate to the following observations and conclusion:

1. The ΔE_a values for the cobalt and copper complexes of 5-(4-phenyl-2-thiazolylazo)-barbituric and -thiobarbituric acids are lower than those of the complexes of 5-(2-thiazolylazo)-barbituric and -thiobarbituric acids. This may be attributed to the π-character of the phenyl group and the associated steric effect. All the cobalt complexes have the stoichiometry 1:1.2 H_2O, with T_d geometry. The copper complexes have the stoichiometry 1:2.n H_2O, where $n = 2$ for all cop-

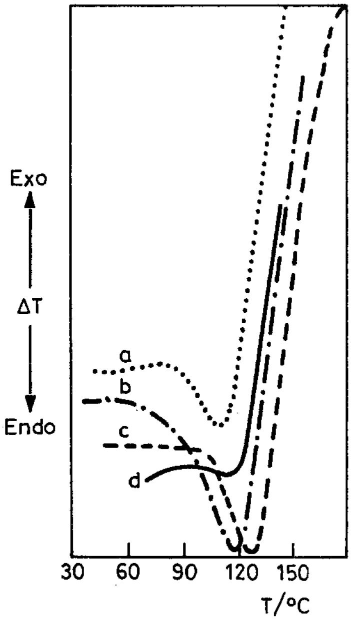


Fig. 1a DTA curves of cobalt complexes derived from, a) L_4 b) L_2 c) L_3 d) L_1

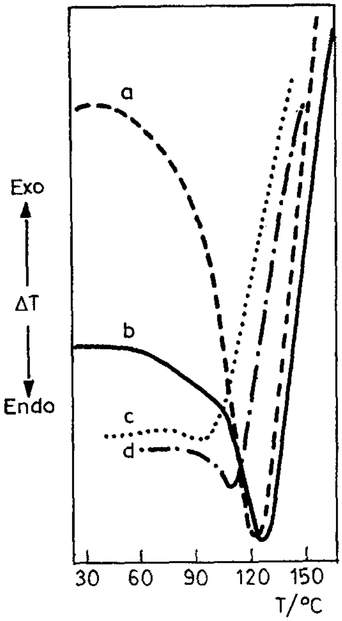


Fig. 1b DTA curves of nickel complexes derived from, a) L_3 b) L_1 c) L_4 d) L_2

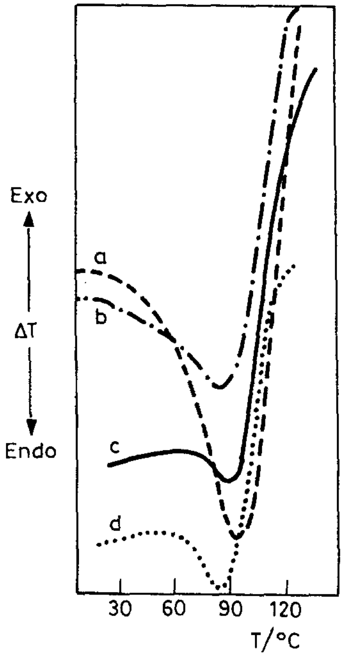


Fig. 1c DTA curves of copper complexes derived from, a) L_3 b) L_2 c) L_1 d) L_4

per complexes except those of 4-phenyl derivatives of barbituric acid and 2-thiobarbituric acid, where $n = 4$, and all have tetragonal geometry. However, the behaviour of the nickel complexes exhibits the opposite trend to that for both cobalt and copper complexes. The mechanism for these systems is controlled by two factors:

(i) The number of water molecules present in the outer sphere of the complex. This number in nickel phenyl compounds is greater than that in the nickel thiazolylazo-barbituric and -thiobarbituric acid complexes. The TG experiment

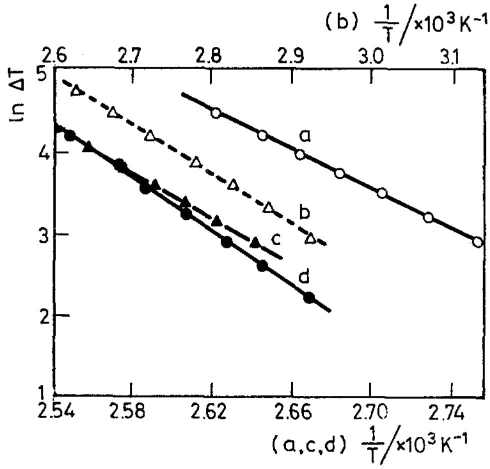


Fig. 2a A plot constructed from DTA curves of cobalt complexes derived from, a) L_4 b) L_2 c) L_3 d) L_1

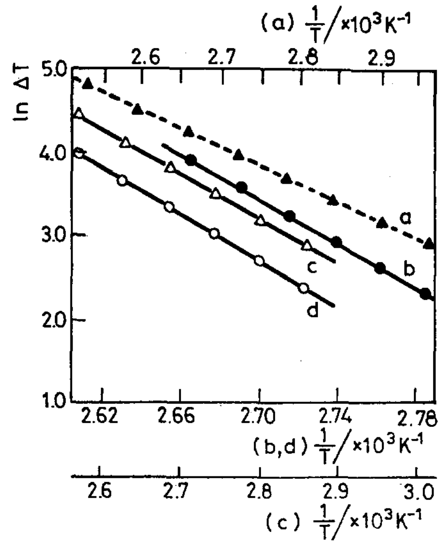


Fig. 2b A plot constructed from DTA curves of nickel complexes derived from, a) L_1 b) L_4 c) L_3 d) L_2

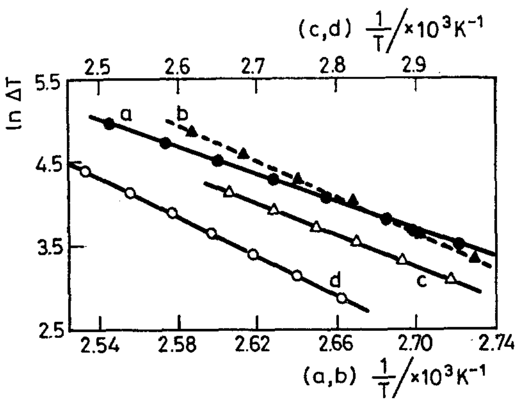


Fig. 2c A plot constructed from DTA curves of copper complexes derived from, a) L_2 b) L_3 c) L_4 d) L_1

on the bimetallic nickel complex ($Ni_2L{\cdot}6H_2O$) of 5-(2-thiazolylazo)-2-thiobarbituric acid gave a 9.25% loss in weight, which indicates that these complexes contain 2 molecules of water in the outer sphere.

(ii) The thermal curves of the bimetallic nickel complexes appeared at higher temperatures by (≈ 20°–25 °C) and with sharper peaks, at 125° and 130 °C, than those of the nickel phenyl complexes. Thus, the process of dehydration of the bimetallic complexes is more sterically hindered and needs higher temperatures than for those of the phenyl compounds. The theoretical weight loss for the proposed formula is 9.4%.

2. The metal complexes under investigation gave two types of reaction mechanism as concerns the order:

(i) first-order for all metal complexes of 5-(2-thiazolylazo)-barbituric and 5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acids;

(ii) first-order reactions for the metal complexes of 5-(4-phenyl-2-thiazolylazo)-barbituric acid and 5-(2-thiazolylazo)-2-thiobarbituric acid.

3. In general, the activation energies follow the sequence

(i) Co > Cu > Ni for complexes of 5-(2-thiazolylazo)-barbituric and -thio-barbituric acids;

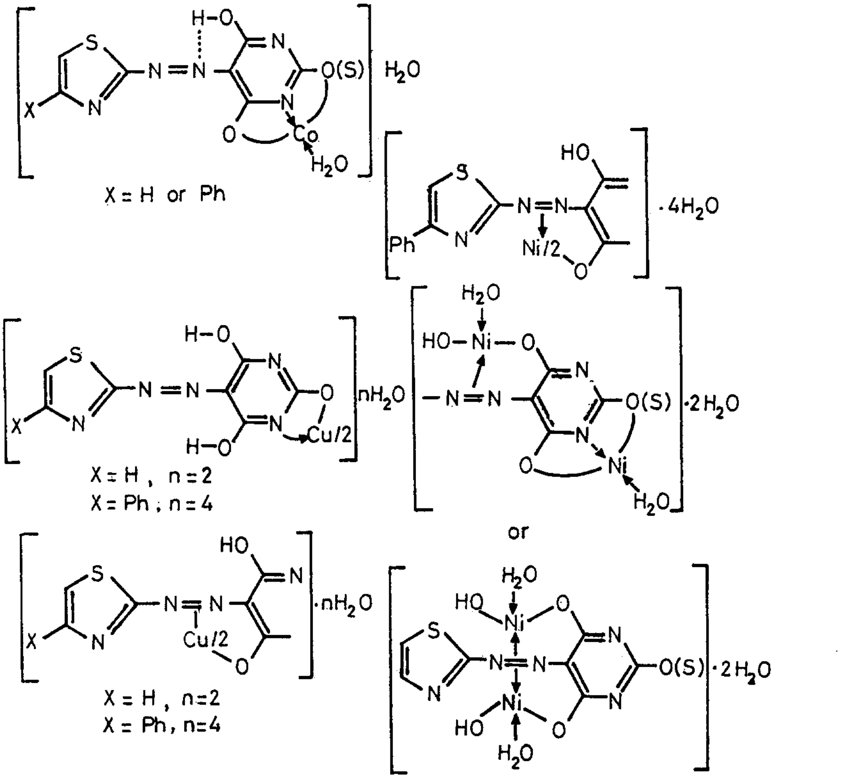
(ii) Ni > Co > Cu for complexes of 5-(4-phenyl-2-thiazolylazo)-barbituric and thiobarbituric acids. The first series may arise from the dehydration process, decreasing with increasing radius of the metal [22]. The activation energy values for the bimetallic nickel complexes are probably due to strong ligand field properties. However, the data for the second series may be attributed to the steric effect of the phenyl group strongly affecting the dehydration of the metal complexes. In spite of the fact that the numbers of water molecules for the nickel and copper phenyl complexes are equal (n = 4), but $\Delta E_{Ni} > \Delta E_{Cu}$. This is probably due to the electronic configurations of Cu (d^9) and Ni (d^8), with one and two unpaired electrons, respectively, where the ligands have a weak field property [23].

Table 3 DTA-activation energies and the reaction orders of thiazolylazo-pyrimidine derivative complexes

Complex		ΔE_a / kJ·mol^{-1}	Order
Cobalt			
5-(2-thiazolylazo)-barbituric acid	L_1	132.05	1.18
5-(4-phenyl-2-thiazolylazo)-barbituric acid	L_2	43.07	2.07
5-(2-thiazolylazo)-2-thiobarbituric acid	L_3	111.13	2.00
5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid	L_4	95.26	1.22
Nickel			
5-(2-thiazolylazo)-barbituric acid	L_1	55.17	1.26
5-(4-phenyl-2-thiazolylazo)-barbituric acid	L_2	105.47	1.70
5-(2-thiazolylazo)-2-thiobarbituric acid	L_3	44.87	1.85
5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid	L_4	112.35	1.24
Copper			
5-(2-thiazolylazo)-barbituric acid	L_1	97.56	1.23
5-(4-phenyl-2-thiazolylazo)-barbituric acid	L_2	27.71	1.16
5-(2-thiazolylazo)-2-thiobarbituric acid	L_3	85.63	1.98
5-(4-phenyl-2-thiazolylazo)-2-thiobarbituric acid	L_4	78.12	1.11

4. The energies of activation for the thio compounds are lower than those of the oxygen homologues for all complexes (except that the nickel and copper phenyl complexes showed a reverse character), due to the electro-negativity difference between oxygen and sulphur. However, the thio complexes absorb at a longer wavelength than do the oxygen homologues, where the thio complexes are structurally more conjugated and more stable than those of oxygen. Alternatively, the dehydration processes for the former compounds are less marked than those for the latter, leading to a decreased ΔE_a for the thio compounds. This explains the variation in the order of reaction value.

The following structures are proposed for the metal complexes:



References

1 W. C. Cutting, Handbook of Pharmacology, 3rd ed., Meredith Company, New York 1967.

2 A. N. Cost and I. I. Gradbery, Progress in Pyrazole Chemistry, Advances in Heterocyclic Chemistry, (Edited by A. R. Katritzky and A. J. Boulton), Vol. 6, Academic Press, New York 1966, p.348.

3 K. Ueda, N. Kobayashi and Y. Yamamoto, Analyst, 111 (1986) 733.

4 V. M. Ivanov, O. M. Vilkova and A. I. Busev, Zh. Anal. Khim., 33 (1978) 716; C.A. 89 (1978) 99082a.

5 J. Ciba and M. Langova, Colln. Czech. Chem. Commun., 38 (1973) 3405.
6 L. Sommer and L. Janoscova, Colln. Czech. Chem. Commun., 39 (1974) 101.
7 H. V. Nguyen and V. M. Ivanov, Zh. Anal. Khim., 36 (1981) 1953; C.A. 95 (1981) 27826t.
8 V. M. Ivanov and H. V. Nguyen, Zh. Anal. Khim., 37 (1981) 171; C.A. 95 (1981) 45271h.
9 I. N. Glushkova and V. K. Semichaev, Anal. Khim., 3 (1980) 11; C.A. 92 (1980) 131580c.
10 G. Nakagawa and H. Wada, Talanta, 20 (1973) 829.
11 V. Chromy and J. Vrestal, Chem. List, 60 (1966) 1537.
12 S. Murata, G. Nakagawa and K. Kodama, Japan Analyst, 23 (1974) 242; C.A. 81 (1974) 44886v.
13 V. Miketukova and R. W. Frei, J. Chromat., 47 (1970) 427.
14 M. S. Masoud, M. A. El-Dessouky, F. A. Aly and S. A. Abou El-Enein, Trans. Met. Chem., 15 (1990) 443.
15 A. I. Vogel, "Practical Organic Chemistry", 3rd ed., Longmans, 1961.
16 H. M. Langova and L Sommer, Talanta, 16 (1969) 681.
17 G. Schwarzenbach, "Complexometric Titration", translated by H. Irving Methuen Co., London 1957.
18 M. S. Masoud, S. S. Haggag, E. M. Soliman and M. E. El-Shabasy, J. Mater. Sci., 26 (1991) 1109.
19 G. M. Bancroft and H. D. Gesser, J. Inorg.Nucl. Chem., 27 (1965) 1537.
20 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, (1966) 1229.
21 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
22 M. S. Masoud, S. A. Abou El-Enein and E. El-Shereafy, J. Thermal Anal., 37 (1991) 365.
23 M. S. Masoud, A. M. Donia and S. S. Abou El-Enein, Thermochim. Acta, 161 (1990) 217.

Zusammenfassung — Anhand thermischer Untersuchungen wurde die Stereochemie von Kobalt(II)-, Nickel(II)- und Kupfer(II)komplexen mit den Liganden 5-(2-Thiazolylazo)-barbitursäure und -thiobarbitursäure untersucht. Es wurden die Reaktionsordnungen und die Aktivierungsenergien ermittelt. Die Ergebnisse wurden unter verschiedenem Aspekt interpretiert, im besonderen Hinblick auf den elektronischen Charakter des Substituenten.